

## Mineralogical and geochemical effects due to hydrothermal alteration in the Los Azufres geothermal field, Mexico

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### ABSTRACT

*To investigate the effects of hydrothermal alteration on the chemistry of volcanic rocks, we analyzed the whole rock chemical composition (major and trace elements, including rare-earth elements – REE) of two distinct portions of a drill well core sample from the Los Azufres geothermal field, Mexico. This highly hydrothermally-altered sample allowed us to study, for the first time, the mineralogical and chemical effects imposed by hydrothermal alteration on the mm scale in this important geothermal system. Mineralogically, hydrothermal alteration in the sample is mainly represented by chloritization of primary olivine and pyroxene, argillitization of primary plagioclase, as well as banded chlorite and quartz, with significant amounts of epidote and hematite. The “altered” part of the sample contains intensely altered remnants of the fresh rock, which show intense silicification, hematization, and dissolution boundaries. Most major and trace elements were mobilized from the original rock. Major element composition reflects the silicification, chloritization, and epidotization processes taking place in the geothermal system. The rare-earth elements La and Ce, as well as Yb and Lu were probably partially re-deposited during alteration. The positive anomaly of Eu may suggest that Eu is being concentrated in hydrothermal epidote after its release from plagioclase to the geothermal fluid. The high-field strength elements such as Zr, Ti, and P, show as well significant hydrothermal alteration-related decrease in the highly-altered rock. The geothermal fluid responsible for this hydrothermal alteration was probably oxidizing, of high temperature (>250° C), and enriched in REE and other trace elements.*

*Key words: geothermal systems, element mobility, water-rock interaction, HFSE, REE, Los Azufres, Mexican Volcanic Belt, Mexico.*

### RESUMEN

*Los efectos de los procesos de alteración hidrotermal en la composición química de rocas volcánicas fueron investigados por medio del análisis químico de roca total (elementos mayores y traza, incluyendo los elementos de las tierras raras) de dos partes diferentes de un mismo fragmento de núcleo de pozo proveniente del campo geotérmico de Los Azufres, México. Esta muestra, con intensa alteración hidrotermal, nos permitió estudiar por primera vez los efectos mineralógicos y químicos impuestos por la alteración en una escala de milímetros para este importante sistema hidrotermal. Desde el punto de*

*vista mineralógico, la alteración hidrotermal de la muestra está evidenciada por la cloritización de olivino y piroxeno primarios, la alteración de plagioclasa primaria a minerales arcillosos, la presencia de clorita y cuarzo en bandas, así como la presencia de abundante epidota y hematita. La porción alterada de la muestra contiene un remanente intensamente alterado de la roca fresca, el cual presenta silicificación intensa, hematización y bordes de disolución. La mayoría de los elementos mayores y traza fueron movilizados de la roca original. La concentración de los elementos mayores es un reflejo de los procesos de silicificación, cloritización y epidotización que afectaron a la roca. Los elementos de las tierras raras La y Ce, así como Yb y Lu, fueron parcialmente redepositados durante la alteración. La anomalía positiva de Eu sugiere que este elemento fue concentrado en la epidota después de haber sido extraído por el fluido geotérmico desde la plagioclasa. Los HFSE como Zr, Ti y P muestran, de la misma manera, importantes reducciones en su concentración relacionadas con la alteración. El fluido geotérmico responsable de esta alteración hidrotermal fue probablemente oxidante, de alta temperatura (>250° C) y enriquecido en tierras raras y otros elementos traza.*

*Palabras clave: sistemas geotérmicos, movilidad de elementos, interacción agua-roca, HFSE, REE, Los Azufres, Cinturón Volcánico Mexicano, México.*

## INTRODUCTION

The Los Azufres geothermal field (LAGF) is located in the central part of the Mexican Volcanic Belt (MVB; Figure 1), approximately 200 km northwest of Mexico City. The LAGF has been extensively explored and developed since 1975. Nowadays, it represents the second most important geothermal field in Mexico, with a total installed capacity for electricity production of about 100 MW (Gutiérrez-Negrín and Quijano-León, 2005).

Even though the Los Azufres area has been the focus of numerous geological, hydrogeological, and geophysical studies (see Verma *et al.*, 2005 and references therein), the geochemical composition of rocks has received relatively less attention. Hydrothermal alteration at the LAGF has been described, among others, by Cathelineau *et al.* (1985) and Torres-Alvarado (2000, 2002). A purely mineralogical study of samples from wells Az-5, Az-28, and Az-31, based on X-ray diffraction analysis, was recently carried out by Pandarinath *et al.* (2006), which, however, presented no chemical data to characterize the related chemical effects of hydrothermal alteration. Geochemical studies from the LAGF have reported major and a few trace elements (Dobson and Mahood, 1985; Cathelineau *et al.*, 1987, 1991; Pradal and Robin, 1994; Torres-Alvarado and Satir, 1998), whereas only Cathelineau *et al.* (1987) and Torres-Alvarado and Satir (1998) discussed hydrothermal alteration effects in the chemical composition of rocks.

Recently, Verma *et al.* (2005) reported a systematic study of the hydrothermal alteration effects for major and trace elements as well as Sr, Nd, and Pb isotopic compositions in rocks from the LAGF, comparing the chemical composition of outcropping (*i.e.*, fresh) rocks to that of relatively more-altered (*i.e.*, shallow <1000 m depth) ones. This comparison was based on the assumption that the shallow, hydrothermally-altered rocks had a “before-alteration” chemistry very similar to the chemical composition of the surface rocks from the LAGF. Using a strict statistical

methodology, these authors showed that significant element mobility has taken place in rhyolitic rocks at the LAGF, especially for the alkalis Na and K, the high-field strength elements Zr, Ti, and P, as well as for Pb and Nd isotopic ratios. Thus, Verma *et al.* (2005) necessarily based their conclusions on the statistical comparison of the chemical composition of fresh rocks (from the surface) to that of the altered ones (from the shallower part of the geothermal field) due to the unavailability (at that time) of a single volcanic rock which could show both fresh and altered portions, and consequently, could allow us to quantify the chemical changes imposed by hydrothermal alteration processes at a much shorter scale. In other words, the existence of such a single volcanic rock would eliminate the necessity of the assumption (implicit in Verma *et al.*, 2005) that prior to the alteration process, the shallow drill well rocks, on the average, had the same major and trace element composition as the same type of surface rocks from the LAGF area.

We report here, for the first time for the LAGF and probably for any geothermal system in the world, a comparative geochemical study between a nearly fresh (or less-altered) rock and its “highly” altered equivalent, both coming from a single core sample of well Az-48 at 2,678 m along-the-well depth. Although the study of a single rock sample can not be considered as representative for all rock units present at the LAGF, it is pertinent to note that such a methodology (study of a single rock sample having both “fresh” and “altered” parts) has been highly successful to study the chemical and isotopic effects of low-temperature seawater alteration in oceanic basalts (Verma, 1981, 1992; Jochum and Verma, 1996). These results on alteration effects have been widely used by other researchers, who have cited these references in their studies of ocean-floor rocks (see *e.g.*, Borisova *et al.*, 2001), ocean-island and island-arc volcanism (*e.g.*, Kersting and Arculus, 1995; Nikolaeva, 1997), ophiolites (*e.g.*, Hatzipanagiotou and Tsikouras, 2001; Srivastava *et al.*, 2004; Tsikouras *et al.*, 2006), hydrothermal alteration (*e.g.*, Kikawada *et al.*, 2001),

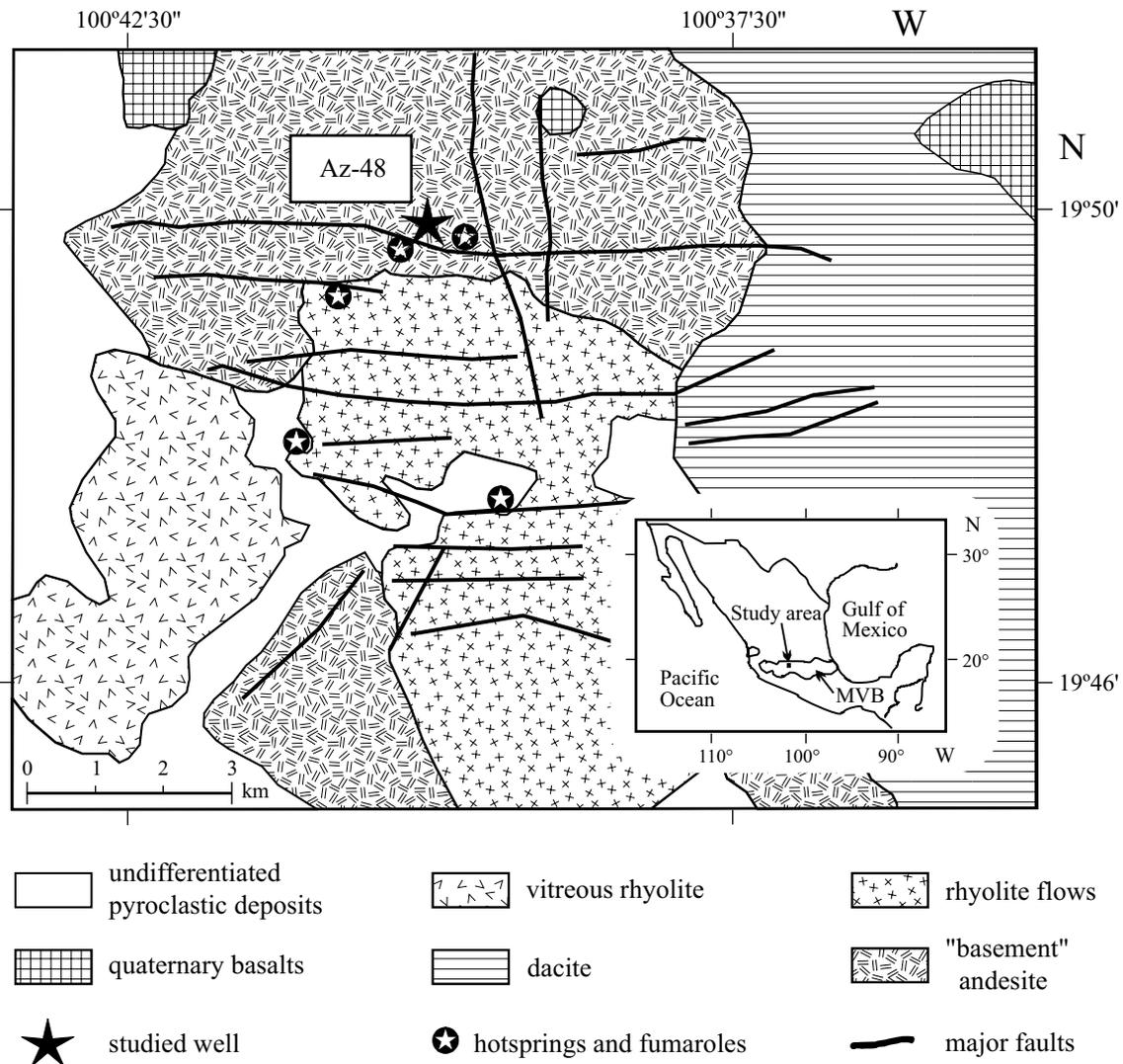


Figure 1. Simplified geologic map of the Los Azufres geothermal field (modified after Dobson and Mahood, 1985). MVB: Mexican Volcanic Belt.

older Precambrian rocks (*e.g.*, Srivastava and Singh, 2004; Kamber *et al.*, 2003), subduction and recycling processes (*e.g.*, Kamber and Collerson, 2000), and Earth's mantle evolution (*e.g.*, Hofmann and White, 1983; Geist *et al.*, 1986; Ren *et al.*, 2006).

The special rock sample from the LAGF reported in this work, allowed us to observe at mm scale the mineralogical changes caused by hydrothermal alteration and to quantify the chemical changes imposed to this single volcanic rock after alteration. Petrographic studies and geochemical analyses of major, several trace elements including the rare-earth elements (REE) and high-field strength elements (HFSE) presented in this study helped us: (1) to describe mineralogical changes that the fresh rock has undergone due to hydrothermal alteration; (2) to study compositional variations of the rock; and (3) to obtain a better understanding of the water/rock interaction processes occurring in this active hydrothermal system.

## GEOLOGICAL SETTING

Los Azufres is one of the several Pleistocene silicic volcanic centers with active geothermal systems in the Mexican Volcanic Belt (MVB; Dobson and Mahood, 1985; Verma, 1985; Anguita *et al.*, 2001). The volcanic rocks at the Los Azufres have been studied by different workers (Cathelineau *et al.*, 1987; Dobson and Mahood, 1985; López Hernández, 1991). Geologically, two principal units can be distinguished (Figure 1): (1) a 2,700 m thick interstratification of lava flows and pyroclastic rocks, of andesitic to basaltic composition with ages between 18 and 1 Ma (Dobson and Mahood, 1985), forming the local basement; and (2) a silicic sequence which partially overlies the mafic unit, characterized by rhyodacites, rhyolites and dacites with ages between 1.0 and 0.15 Ma and a thickness up to 1,000 m. The mafic unit provides the main aquifer with fluid flow through fractures and faults, sometimes reaching the surface

in the form of hydrothermal manifestations, accompanied by strong kaolinitization and silicification.

Three different fault systems, which confer secondary permeability to the geological units, can be distinguished (Figure 1; Ferrari *et al.*, 1991): NE-SW, E-W, and N-S. The E-W system is the most important one for geothermal fluid circulation. Geothermal manifestations (fumaroles, solfataras, and mudpits), geophysical anomalies, as well as important geothermal production zones (the intersection between faults and geothermal wells) are related to this fault system.

The geothermal fluids at the LAGF are sodium-chloride rich waters with high CO<sub>2</sub> and H<sub>2</sub>S contents, and a pH around 7.5 (Birkle *et al.*, 2001). Average Cl<sup>-</sup> contents are 3,100 mg/kg and CO<sub>2</sub> can attain as much as 90% of the total gas phase. Fluid temperatures can reach values as high as 320°C; however, 240 to 280°C are normally observed temperatures in the field.

Hydrothermal alteration has affected most rocks in the geothermal field to varying extent. Studies of hydrothermal alteration at the LAGF carried out, among others, by Cathelineau *et al.* (1985), and Torres-Alvarado (2002) have shown that partial to complete hydrothermal metamorphism has occurred. Most important alteration assemblages with increasing depth are: argillitization/silicification, zeolite/calcite formation, sericitization/chloritization, and chloritization/epidotization.

## SAMPLING AND ANALYTICAL DETAILS

### Sampling and sample preparation

The studied sample was taken from a drill core from well Az-48 (coordinates: 100°39'48" W, 19°49'27" N) at 2,678 m depth along drilling direction (Figure 1). It was carefully divided into two pieces avoiding contamination between the highly-altered portion of the core and the less-altered rock (Figure 2a). All handpicked pieces were cleaned with distilled water to remove any adhering dust particles, oven dried at about 60°C, and pulverized for geochemical analyses. For petrographic purposes, a standard thin section was carefully prepared to include the contact area between the highly-altered and the less-altered portions of the sample, together with the remnant of the original rock enclosed by the altered section (see central bottom part of sample in Figure 2a).

### Analytical methods

Minerals present in both altered and fresh portions of the rock sample were identified by X-ray diffraction. The powdered samples were scanned from 2 to 60° 2θ in a Bruker X-ray diffractometer (Model-D8 ADVANCE) with Ni-filtered Cu Kα radiation at the Ocean Science

and Technology Cell (Marine Geology and Geophysics), Mangalore University, India.

Major elements were analyzed by X-ray fluorescence spectrometry (XRF) on duplicate lithium metaborate fused discs, using a Philips MAGIX PRO spectrometer at the Centro de Investigación en Energía, Universidad Nacional Autónoma de México (procedure similar to the one reported by Verma *et al.*, 1992, except that here we explicitly took into account the loss on ignition (LOI) values for the preparation of fused disks so that the final XRF results are obtained on an anhydrous basis). The REE and other trace elements were measured by inductively-coupled plasma mass spectrometry (ICP-MS) at GeoForschungsZentrum Potsdam, Germany (for details about the analytical procedure see Dulski, 2001). For analytical accuracy estimates, the chemical analyses of International Reference Material JR-1 (Imai *et al.*, 1995) and the internal standard TUX07 (Verma, 2006) are reported in Table 1. Precisions were better than these accuracy estimates.

## RESULTS AND DISCUSSION

### Petrography

The relatively fresh rock sample in hand specimen is an aphanitic volcanic rock, dark gray in color (Fig. 2a). Under the microscope it shows a pilotaxitic to porphyritic texture. Phenocrysts of olivine and pyroxene (probably augite, as reported by Torres-Alvarado, 2000, for similar basaltic rocks from the LAGF) are embedded in a matrix of microlitic plagioclase, zircon, apatite, and magnetite, which is mostly altered to hematite. Olivine and pyroxene phenocrysts are totally altered to chlorite and hematite, frequently as pseudomorphs after the primary minerals. Microlitic plagioclase is only partially altered to clay minerals allowing us to estimate, for this sample, a degree of alteration of about 30% (using charts for estimating area % of minerals in thin section; Shelley, 1992). Several chlorite and quartz veins cut the sample, showing thickness between ~1.0 and ~0.1 mm. A chlorite vein was observed to be additionally cut by a vein of cryptocrystalline quartz (Figure 2b), providing evidence for the existence of at least two fluid flow events during hydrothermal alteration precipitation.

The highly-altered section of the sample (altered to nearly 100%) is aphanitic as well, showing a light greenish-gray color. Under the microscope, this rock section is built up by banded chlorite, clay minerals, and cryptocrystalline to microcrystalline anhedral quartz. They all may contain anhedral to subhedral epidote crystals and rarely some small amphibole crystals of acicular texture. Opaque minerals (mainly hematite) are also present in the altered sample, although in lesser amounts than in the original one (Figure 2c). Within this highly-altered sample section, a remnant of the less-altered rock is present, showing original plagioclase crystals to be totally altered to cryptocrystalline quartz or

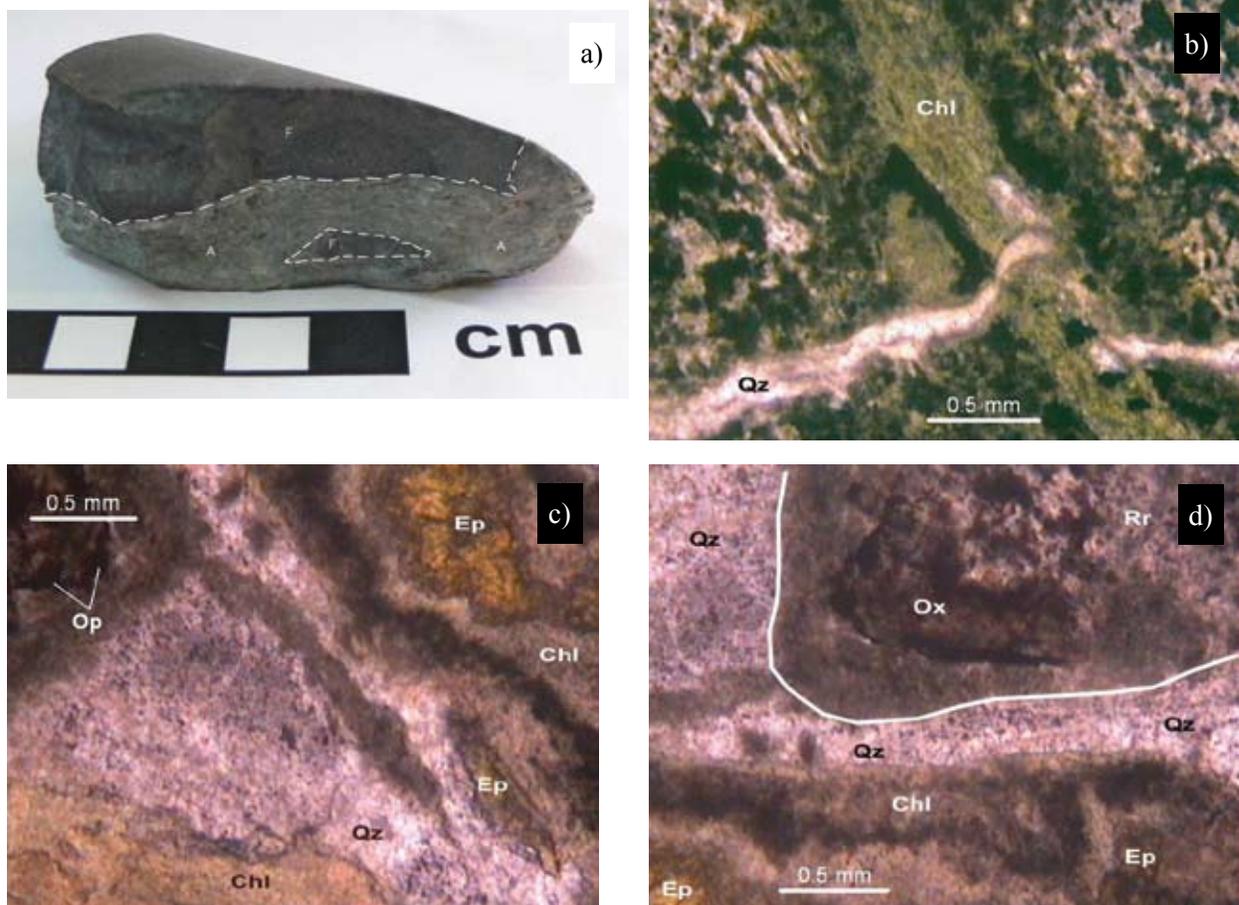


Figure 2. a: Analyzed core sample from well Az-48 at 2,678 m depth, showing the relatively fresh rock (or less-altered rock; F) along the alteration zone (A); the section showing the “fresh” rock remnant contained in the altered zone was selected for thin section preparation (e.g. petrographic studies); b: quartz vein cutting a chlorite vein, evidencing the occurrence of two different fluid flow events for hydrothermal alteration processes (5X, || nichols); c: banded chlorite and cryptocrystalline quartz containing intergrowths of subhedral epidote (5X, || nichols); d: detail of rock remnant (graphically separated by continuous white line) being dissolved into the hydrothermal alteration area; note strong silicification and hematization of original minerals (5X, || nichols). Abbreviations are: Ep: epidote, Qz: quartz, Chl: chlorite, Ox: iron oxides, Op: opaque minerals, Rr: rock remnant.

clay minerals, as well as more abundant hematite in the matrix (comparing its abundance in the less-altered rock; Figure 2d). Close to the quartz or chlorite veins, the rock shows intense silicification along with dissolution, showing that chlorite and clay minerals contribute to the complete replacement of the original volcanic rock (Figure 2d).

The X-ray diffraction analysis supports the petrographic observations. The less-altered rock sample shows a dominant proportion of plagioclase, followed by quartz and chlorite. Plagioclase is probably of labradoritic composition, as suggested by the predominant peak at 3.18 Å, and supported by plagioclase microprobe analyses ( $An_{52-78}$ ) reported by Torres-Alvarado (2000) for similar basaltic rocks from other wells of the LAGF. Epidote, hematite, and amphibole are present in minor quantities. Tremolite is probably the amphibole phase present in the sample, as indicated by its main peak at 8.3 Å, and by the chemical composition reported by Torres-Alvarado (2000) for amphibole crystals observed in other wells at the LAGF. On the other hand,

the X-ray diffraction analysis of the highly-altered part of the rock sample shows a predominant presence of quartz and, in lower proportions, of K-feldspars, plagioclase, and amphibole. The hydrothermal plagioclase may have an albitic composition, as suggested by the main peak at 3.14 Å, and microprobe chemical analyses reported for hydrothermal plagioclase ( $Ab_{87-98}$ ) from other areas of the LAGF (Torres-Alvarado, 2000). Though the hydrothermal amphibole is present in both the less-altered and the highly-altered portions of the sample, its content is more elevated in the highly-altered portion.

### Chemical composition

The actually measured major and trace element abundances for the relatively fresh (48-2678-F) and the highly-altered (48-2678-A) samples are given in Table 1. According to the TAS classification (Le Bas *et al.*, 1986; Le Bas, 2000),

Table 1. Chemical composition of studied samples from the Los Azufres geothermal field (LAGF).

Sample	48-2678-F	48-2678-A	TUX07(m)	TUX07(r)	JR1(m)	JR1(r)
Rock type	B, subal		BSN, mnp		R	
SiO <sub>2</sub>	49.52	72.82	42.69	42.34	76.50	76.51
TiO <sub>2</sub>	2.39	0.03	1.68	1.82	0.11	0.11
Al <sub>2</sub> O <sub>3</sub>	16.64	3.51	11.74	11.83	13.01	13.01
Fe <sub>2</sub> O <sub>3</sub> <sup>T</sup>	12.30	8.12	13.10	12.57	0.90	0.90
MnO	0.16	0.23	0.20	0.20	0.10	0.10
MgO	7.11	7.47	14.81	14.30	0.12	0.12
CaO	7.05	7.49	11.68	12.68	0.68	0.68
Na <sub>2</sub> O	3.15	< 0.01	2.53	2.77	4.08	4.08
K <sub>2</sub> O	0.97	0.30	0.75	0.69	4.47	4.47
P <sub>2</sub> O <sub>5</sub>	0.70	0.02	0.82	0.80	0.02	0.02
Total	99.99	99.99	100.00	100.00	99.99	100.00
La	23.5	5.73	-	-	19.6	19.7
Ce	53.5	10.5	-	-	46.1	47.2
Pr	7.02	1.23	-	-	5.86	5.58
Nd	30.3	5.24	-	-	23.1	23.3
Sm	6.70	1.13	-	-	5.71	6.03
Eu	2.08	1.79	-	-	0.27	0.3
Gd	6.23	1.22	-	-	5.64	5.06
Tb	0.92	0.18	-	-	0.98	1.01
Dy	5.40	1.23	-	-	6.19	5.69
Ho	1.05	0.28	-	-	1.31	1.11
Er	2.86	0.85	-	-	4.08	3.61
Tm	0.39	0.13	-	-	0.64	0.67
Yb	2.43	1.00	-	-	4.56	4.55
Lu	0.36	0.18	-	-	0.70	0.71
Rb	16.0	4.95	-	-	256	257
Sr	601	405	-	-	26.6	29.1
Y	26.3	9.14	-	-	39.0	45.1
Zr	281	3.45	-	-	93.0	99.9
Nb	24.0	0.77	-	-	16.9	15.2
Cs	2.91	0.59	-	-	19.5	20.8
Ba	247	61.7	-	-	42.7	50.3
Hf	5.81	0.08	-	-	4.70	4.51
Ta	1.50	< 0.04	-	-	2.01	1.86
Pb	12.5	18.9	-	-	18.4	19.3
Th	1.90	0.02	-	-	25.5	26.7
U	0.65	0.13	-	-	8.50	8.88

Sample 48-2678-F refers to the less-altered sample, whereas 48-2678-A refers to the highly-altered section of the core sample. Analyses of an “in-house” reference material TUX07 and an international reference material JR1 are reported (m: measured in this work) for analysis quality evaluations, along with the most probable concentrations (r: values recommended by Verma, 2006, for TUX07, and Imai *et al.*, 1995, for JR1). Major element analyses have been adjusted to 100% on an anhydrous basis. B, subal: subalkaline basalt; BSN, mnp: basanite, melanephelinite; R: rhyolite. Fe<sub>2</sub>O<sub>3</sub><sup>T</sup>: total iron expressed as Fe<sub>2</sub>O<sub>3</sub>; rock types defined after the total alkalis vs. silica diagram (Le Bas *et al.*, 1986; Le Bas, 2000), on an anhydrous, 100% adjusted basis and with Fe<sub>2</sub>O<sub>3</sub>/FeO ratio after Middlemost (1989), calculated with the SINCLAS computer program (Verma *et al.*, 2002).

the less-altered rock shows a basaltic composition.

Major elements show a general decrease in the altered sample compared to the less-altered rock. Exceptions to this are SiO<sub>2</sub>, MgO, and MnO, which are important elements incorporated into the highly-altered rock due to silicification, chloritization, and epidotization, respectively (Torres-Alvarado, 2000), in agreement with the importance of these alteration processes in the LAGF (Torres-Alvarado, 2002). Loss of alkalis seems to be an important alteration effect for the LAGF as well, as already pointed out by Verma *et al.* (2005).

Figure 3 shows the differences in the REE chemical

compositions between both samples, normalized to the chondritic composition (values from McDonough and Sun, 1995). All REE are present at lower concentrations in the highly-altered rock compared to the less-altered one (Table 1, Figure 3). Whereas the original rock shows a smooth, light REE-enriched pattern with no Eu anomaly (typical of surface basaltic rocks from the LAGF; Verma *et al.*, 2005), the highly-altered rock shows lower rock/chondrite concentration ratios for all elements, with a remarkable positive Eu anomaly. For the highly-altered rock, light REE (LREE), particularly La and Ce, show higher concentration compared to other LREE (Table 1), indicated by a negative slope for

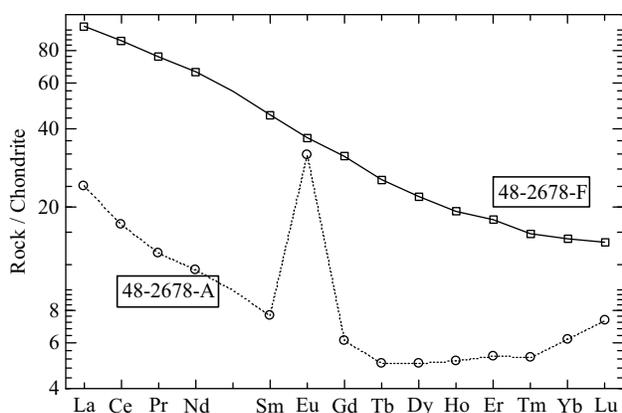


Figure 3. REE chemical composition (log scale) of the analyzed samples, normalized to the chondritic abundances (values from McDonough and Sun, 1995). Sample 48-2678-F refers to the less-altered rock, whereas 48-2678-A refers to the highly-altered section of the core sample.

the REE pattern in the leftmost section (LREE) of the diagram (Figure 3). Yb and Lu present the opposite behavior, as their normalized concentration ratios are relatively higher than the rest of HREE (Table 1), represented by a positive trend at the rightmost section of the diagram (Fig. 3).

For quantitatively evaluating water-rock interaction processes occurring in the field, it would be interesting in future to measure the actual concentration of these elements in the Los Azufres geothermal fluids and hydrothermal minerals. However, based on the available information for the LAGF, REE were possibly partially leached from the

original rock and precipitated again with the hydrothermal alteration in lower concentrations, explaining in this way the generally lower concentrations for all REE, along with the relatively higher concentrations of La and Ce compared to other LREE in the highly-altered sample. A similar process seems to have occurred for heavy REE (HREE), where Yb and Lu show relatively higher concentrations in the highly-altered sample. This observation stresses the caution that has to be taken when assuming REE as relatively immobile under hydrothermal conditions and emphasizes the necessity of determining REE concentrations of the geothermal fluids at the LAGF for a better understanding of the alteration processes.

Eu in the highly-altered sample reaches almost the same concentration as in the fresh rock. This positive Eu anomaly has been also observed in some hydrothermal ore deposits (e.g., Palacios *et al.*, 1986) and in hydrothermal fluids from mid-ocean ridges (e.g., Klinkhammer *et al.*, 1994). Klinkhammer *et al.* (1994) opined that the partition of  $\text{REE}^{3+}$  and  $\text{Eu}^{2+}$  is dominated by the chemical substitution for  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  in plagioclase, respectively, during the transition from An-rich plagioclase to Ab-rich hydrothermal plagioclase. Furthermore, Palacios *et al.* (1986) considered epidote as the principal hydrothermal mineral containing REE, and pointed out that its REE concentration is controlled by the REE content in the hydrothermal fluid with probably oxidizing characteristics. Both the previous statements agree with our results, suggesting a predominant role for epidote at the LAGF, allocating REE which have been perhaps mobilized from plagioclase by hydrothermal altera-

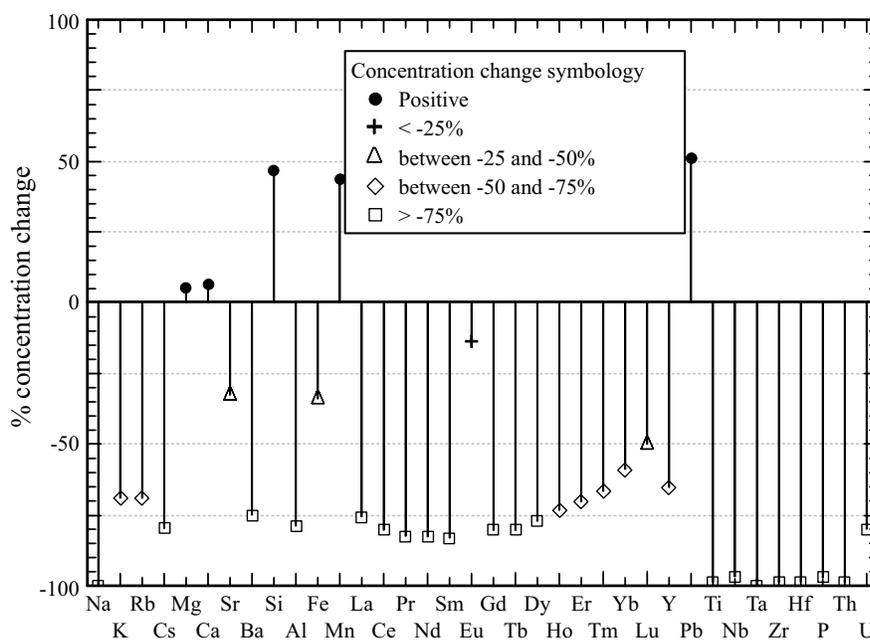


Figure 4. Elemental changes between the highly-altered and the less-altered sample for all analyzed elements. Concentration changes were calculated using the relation  $100 \cdot (C_A^i - C_F^i) / C_F^i$ , where  $C_A^i$  is the concentration of element  $i$  in the highly-altered sample, and  $C_F^i$  is the concentration of the same element in the less-altered sample. Different symbols shown as inset indicate different ranges of concentration change. Note that elements were arranged principally according to their atomic number, rather than their petrogenetic behavior.

tion processes. According to Palacios *et al.* (1986) this could suggest an oxidizing, REE-enriched geothermal fluid, which could be the source for the precipitation of hydrothermal assemblages at the LAGF. Abundant hydrothermal hematite supports this hypothesis. The fact that Eu is not considerably depleted in the highly-altered rock may indicate that Eu was retained in hydrothermal epidote and albite. However, some other studies have shown that REE mobilization may also take place under reducing conditions (*e.g.*, Parr, 1992; Jiang *et al.*, 2003). The presence of hydrothermal pyrite in other regions of the LAGF reservoir indicates the existence of fluids with relatively low  $fO_2$  (Torres-Alvarado, 2002). Considering this uncertainty, REE chemical analyses of geothermal fluids and hydrothermal minerals in the LAGF are needed to accept or refuse these hypotheses.

Quantitative estimates of the chemical changes between the less-altered and the highly-altered rock samples are presented in Figure 4 (see also Table 1) for all elements analyzed for this work. Only Mg, Ca, Si, Mn, and Pb increased in their concentration in the highly-altered portion of the rock as a result of hydrothermal effects. Si enrichment of about 50% observed in the highly-altered rock (as compared to the less-altered one) reflects the main silicification process that occurred in this sample (see also Figure 2d). Higher Mn concentration in the altered portion of the sample seems to reflect Mn enrichment related to the presence of Mn-rich epidotes in the LAGF, as analyzed by Torres-Alvarado (2000). Chlorite was observed as the most widespread mineral in the highly-altered zone of the sample. Its presence in the LAGF agrees with the higher contents of Mg in the highly-altered sample, because chlorites from the LAGF show variable Mg concentration ranging between Fe-clinochlore and Mg-chamosite (Torres-Alvarado, 2000).

Significant losses were observed for most of the analyzed elements (Figure 4). About 75% of the alkalis were removed from the fresh rock by means of hydrothermal alteration. Na loss might be even more significant, considering that it was not possible to chemically quantify this element in the highly-altered rock because it was found to be under the detection limit of our XRF analytical procedure (~0.01%; Table 1). Sr and Ba behaved differently than the other alkaline-earth elements (Mg and Ca, which are enriched in the highly-altered rock), and showed decrements of about 30 and 75%, respectively. In the same way, Al and Fe presented a decrease of about 34 and 79%, respectively. As mentioned above, all REE behaved as a relatively consistent group presenting a decrease (from 50 to 83%) in their concentrations, with the exception of Eu whose decrement reached only about 14%. HREE presented the lowest concentration changes within the REE group.

The highest concentration changes were interestingly observed for the high-field strength elements (HFSE), considered to be immobile during hydrothermal alteration process (*e.g.*, Rollinson, 1993). Ti, Nb, Zr, Hf, P, and Th concentrations decreased to about 100%. In fact, Ta concentration in the highly-altered sample was found to be below

the detection limit (~0.04 ppm) of our ICP-MS procedure, whereas U decreased to about 80%.

Considering that this volcanic rock was altered in different events, as shown by crossed veins of hydrothermal minerals (Figure 2b), it is likely that the rock reacted with hydrothermal fluids at several occasions and, therefore, the alteration processes, which form this alteration mineral assemblages, may have occurred under rather large water/rock ratios (>1). More precise estimates of water-rock ratios will strongly depend on the chemistry of the geothermal fluids. Strong silicification and almost complete replacement of the observed rock remnant (Figure 2d) indicate that fluids had sufficient time to react with this rock. Moreover, the rates of water-rock reactions might have been increased by high temperatures (perhaps higher than 250 °C, as indicated by the presence of hydrothermal epidote and amphibole).

We should emphasize that the hydrothermal alteration conditions observed in this probably unique highly hydrothermally-altered sample cannot be extrapolated to the rest of the field. The geothermal fluid responsible for the hydrothermal alteration in the LAGF may widely vary in trace element composition, both on spatial and temporal basis (Birkle *et al.*, 2001). However, our study indicates that the geothermal fluid could have, besides the expected high concentrations of the alkalis, significantly high concentrations of all REE and HFSE. Again, specific chemical analyses of geothermal fluids and minerals will help to accept or refuse these hypotheses.

Important chemical losses were observed for P, Ti, and Zr, which have been typically considered as immobile elements. Significant decrease is also observed in the concentrations of Hf and Nb. Similar conclusions were recently reached by Verma *et al.* (2005) by statistically comparing the fresh (outcropping) to the hydrothermally-altered rhyolitic rocks from the LAGF. Mobilization of HFSE due to hydrothermal alteration has been reported by several authors (*e.g.* Salvi y Williams-Jones, 1996; Jiang, 2000; Salvi *et al.*, 2000; Jiang *et al.*, 2003). This observation is noteworthy because these elements, especially the HFSE, are widely used for petrogenetic studies; therefore, caution must be exercised for samples which are hydrothermally-altered, such as in older metamorphic terranes.

## CONCLUSIONS

A core sample from well As-48 at 2,678 m along-drill well depth allowed us to study, for the first time for the Los Azufres geothermal field, the mineralogical and chemical variations imposed by hydrothermal alteration processes to a basaltic rock sample.

Mineralogically, banded chlorite and quartz built up the highly-altered part of the rock sample, having significant amounts of epidote, hematite, and calcic amphibole (probably tremolite). The less-altered rock sample has been partially altered as well (~30%), mainly by chloritization

and hematization of olivine and pyroxene phenocrysts, and partial argillization of plagioclase.

Most major and trace elements were mobilized from the original rock. Silicification, chloritization, and epidotization processes account for the major-element composition of highly-altered rock. Most REE, if not all, were probably mobilized by hydrothermal processes. Additionally, La and Ce, as well as Yb and Lu, probably mobilized from the original volcanic rock, were partially re-deposited from geothermal fluids during deposition of hydrothermal minerals, as well as during the alteration of the sample. A remarkable positive anomaly of Eu suggests that this element is being concentrated in hydrothermal epidote after being released from plagioclase to the geothermal fluid. High-field strength elements were mobilized as well during hydrothermal alteration, stressing the necessity of caution using these trace elements for petrogenetic studies of igneous and metamorphic rocks.

The geothermal fluids responsible for this alteration may have been characterized by a high temperature (>250°C, as evidenced by the presence of hydrothermal epidote and amphibole), oxidizing conditions (as suggested by significant amounts of hematite), and enrichment of both REE and HFSE.

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